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In re application of: Hiroto KIDOKORO

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For: **Toner and Method for Producing the Same**

DECLARATION UNDER 37 CFR1.132

Commissioner for Patents  
P.O.Box 1450  
Alexandria, VA 22313-1450

Sir:

I, **Hiroto KIDOKORO**, a citizen of Japan, hereby declare and state:

1. I have a degree in Organic and Polymer Chemistry which was conferred upon me by Graduate School of Science and Engineering, Saitama University, in Saitama, Japan, in 1981.

2. I have been employed by ZEON CORPORATION since 1984 and I have had a total of 8 years work and research experience in Chemistry.

3. I, under my direct supervision and control, have conducted the following experiment:

The undersigned declares that all statements made herein of his/her own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signed this 1 day of April, 2009

Hiroto Kidokoro  
Hiroto KIDOKORO

## EXPERIMENT RESULTS

Production Example 1: Production of a negative charge control resin composition

5        A negative charge control resin (100 parts; weight average molecular weight: 20,000, glass transition temperature: 65°C), obtained by polymerizing 82 % of styrene, 11% of butyl acrylate and 7% of 2-acrylamide-2-methylpropanesulfonic  
10    acid, was dispersed in 24 parts of methyl ethyl ketone and 6 parts of methanol, and they were mixed and kneaded by a roll with cooling. After the resulting mixture was wound on the roll, 100 parts of (C.I. Pigment Red 122, manufactured by  
15    Clariant Int., Ltd.) was gradually added, and 1 part of an ethanol solution of potassium ethoxide (a concentration of 50% by weight) was further added, and they were mixed and kneaded for 1 hour, to manufacture a negative charge control resin  
20    composition. During this period, the clearance between the rolls was initially 1 mm, broadened gradually, to finally to 3 mm, and an organic solvent (a solvent mixture of methyl ethyl ketone P/methanol = 4/1) was added occasionally according  
25    to mixing and kneading condition of the negative charge control resin composition. Furthermore,

0.5 g of the negative charge control resin composition was collected, and 20 ml of water was added to the composition. The mixture was sufficiently shaken and served for measuring pH.

5 The ethanol solution of potassium ethoxide (a concentration of 50% by weight) was added by a small amount until the pH reaches 7.

Toluene was added to a portion of the negative charge control resin thus-obtained to obtain 5%  
10 toluene solution of the negative charge control resin composition. Then, the thus-obtained solution was coated on a glass plate using a doctor blade having a thickness of 30  $\mu\text{m}$  and dried. No particle having a length of at least 0.2  $\mu\text{m}$  by observing the sheet by  
15 optical micrograph.

Further, a water dispersion prepared by dispersing 6 g of the pigment used in 100 ml of ion-exchanged water having a pH of 7 had a pH of 6.7.

20

### Example 1

An aqueous solution containing 6.9 parts of sodium hydroxide (alkali metal hydroxide) dissolved in 50 parts of ion-exchanged water was gradually  
25 added to an aqueous solution containing 9.8 parts of magnesium chloride (water-soluble polyvalent

metallic salt) dissolved in 250 parts of ion-exchanged water, with stirring, to prepare a magnesium hydroxide colloidal dispersion (colloid of hardly water-soluble metal hydroxide). As for the particle distribution of the above described colloid produced, the number average particle diameter D50 (50% cumulative value of the number particle diameter distribution) and D90 (90% cumulative value of the number particle diameter distribution) of the droplets were determined by a particle size analyzer (trade name: SALD 2000A, product of Shimadzu Corporation). The measurement by the particle size analyzer was performed under the following conditions: refractive index = 1.55-0.20i, ultrasonic irradiation time = 5 minutes, and a 10% solution of salt as a dispersion medium during the measurement of droplets.

A polymerizable monomer composition for core comprising 90 parts of styrene, 9.875 parts of butyl acrylate, 0.125 part of glycidyl methacrylate and 10 parts of a master batch that is a negative charge control resin composition obtained in Production Example 1 was dissolved/dispersed to obtain a solution, to which 3 parts of t-dodecyl mercaptan and 10 parts of dipentaerythritol hexamylristate were added, stirred and mixed to be

uniformly dispersed therein to obtain a polymerizable monomer composition for core.

Separately, 2 parts of methyl methacrylate and 100 parts of water were subjected to  
5 finely-dispersing treatment using an ultrasonic emulsifier to obtain an aqueous dispersion of a polymerizable monomer for shell. The particle diameter of the droplets of the polymerizable monomer for shell was determined by a particle size  
10 analyzer (trade name: SALD 2000A, manufactured by Shimadzu Corporation). D90 was found to be 1.6  $\mu\text{m}$ .

The above polymerizable monomer composition for core was poured into the above  
15 colloidal dispersion of magnesium hydroxide (weight of the colloid: 4.0 parts), and the mixture was stirred until droplets became stable. After stabilization of the droplets, 6 parts of t-butyl peroxy-2-ethylhexanoate (trade name: Perbutyl O,  
20 manufactured by NOF Corporation) was added. The resultant monomer mixture was stirred for 30 minutes at 15,000 rpm under high shearing force by means of Ebara Milder (trade name: MDN303V, manufactured by EBARA Corp.) to form finer  
25 droplets of the polymerizable monomer composition for core. The thus-prepared aqueous dispersion

containing the droplets of the polymerizable monomer composition for core was provided into a reactor equipped with agitating blades. The polymerization reaction was initiate at 90°C. At  
5 the time the conversion of the monomer into a polymer reached almost 100%, a reaction product in the reactor was sampled to measure the particle diameter of a core. The core had a particle diameter of 7.3  $\mu\text{m}$ . The above aqueous dispersion  
10 of the polymerizable monomer for shell and 0.2 part of a water-soluble polymerization initiator (trade name: VA-086, manufactured by Wako Pure Chemical Industries, Ltd.)(2,2'-azobis{2-methyl-N-(2-hydroxyethyl)-propi  
15 onamide}) dissolved in 65 parts of distilled water were added to the reactor. After the polymerization reaction was continued for 4 hours, the reaction was stopped, to obtain an aqueous dispersion of core-shell structure toner particles  
20 having a pH of 9.5.

While stirring the aqueous dispersion of core-shell structure toner particles obtained above, the pH of the system was adjusted to 5 or lower by adding sulfuric acid, for 10 minutes at 25°C to refer  
25 as acid-washing. This dispersion was then dehydrated by filtration. Then, 500 parts of

ion-exchanged water was added to form a slurry again and conduct washing with water. Then, the dehydration and water washing procedure was repeated several times. Thereafter, solid content  
5 was separated by filtration and dried with a dryer for 2 days and nights at 45°C, whereby toner particles were obtained.

The dried toner particles were taken out for measurement. The results were that volume  
10 average particle diameter ( $D_v$ ) was 7.5  $\mu\text{m}$ , volume average particle diameter ( $D_v$ )/ number average particle diameter ( $D_p$ ) was 1.19,  $r_l/r_s$  was 1.1, and had a tetrahydrofuran-insoluble content of 0%. Furthermore, the number of pigment particles with  
15 a length of 0.2  $\mu\text{m}$  or more present in 100  $\mu\text{m}^2$  was counted, and the number of pigment particles with a length of 0.2  $\mu\text{m}$  or more in 100  $\mu\text{m}^2$  was found to be 20 pieces.

To 100 parts of the toner particles obtained  
20 above, there was added 0.6 part of colloidal silica (RX-200, manufactured by Nihon Aerosil Co. Ltd.) subjected to a hydrophobicity-imparting treatment. They were mixed by means of a Henschel mixer to prepare a negatively charged toner. The thus  
25 obtained toner for electrostatic charge image development was subjected to evaluation below.



The results are shown in Table 1.

### Example 2

#### (1) Preparation of Parting Agent Dispersion:

5       Ninety parts of styrene and 10 parts of a  
parting agent (Fischer-Tropsch wax, "FT-100", trade  
name; product of Shell MDS Co.) were wet ground  
by means of a media type wet grinding machine to  
prepare a styrene monomer parting agent dispersion  
10   in which the parting agent had been uniformly  
dispersed.

#### (2) Preparation of Quaternary Ammonium Salt Group-containing Copolymer:

15       After a 3-liter flask was charged with 900  
parts of toluene, 88 parts of styrene, 4 parts of  
butyl acrylate, 8 parts of dimethylaminoethylbenzyl  
methacrylate chloride and 2 parts of  
azobisdimethylvaleronitrile and reacted at 80°C for  
20   8 hours under stirring, the solvent was removed by  
distillation under reduced pressure to obtain a  
quaternary ammonium salt group-containing  
copolymer ( $M_w=30,000$ , quaternary ammonium salt  
group-containing monomer unit=8.0 wt. %).

(3) Preparation of Polymerizable Monomer  
Composition (liquid mixture):

Twenty parts of the parting agent dispersion  
(containing 2 parts of the parting agent and 18  
5 parts of styrene) prepared above, 65 parts of  
styrene, 17 parts of n-butyl acrylate, 5 parts of a  
magenta pigment (Pigment Red 122), 1 part of the  
quaternary ammonium salt group-containing  
copolymer and 0.3 parts of divinylbenzene were  
10 stirred and mixed by an ordinary stirring apparatus  
and then uniformly dispersed by a media type  
dispersing machine, thereby obtaining a  
polymerizable monomer composition.

15 (4) Preparation of Dispersing Agent-containing  
Aqueous Dispersion Medium:

An aqueous solution with 5.8 parts of sodium  
hydroxide (alkali metal hydroxide) dissolved in 50  
parts of ion-exchanged water was gradually added  
20 to an aqueous solution with 9.5 parts of magnesium  
chloride (water-soluble polyvalent metallic salt;)  
dissolved in 250 parts of ion-exchanged water under  
stirring to prepare a dispersion of magnesium  
hydroxide colloid (colloid of hardly water-soluble  
25 metal hydroxide).

### (5) Suspension Polymerization:

The polymerizable monomer composition obtained above was poured into the colloidal dispersion of magnesium hydroxide obtained above, 5 the mixture was stirred for several minutes by an ordinary stirrer until droplets of the polymerizable monomer composition became stable, and 4 parts of a polymerization initiator, t-butyl peroxy-2-ethylhexanoate (product of Nippon Oil & 10 Fats Co., Ltd.) was then dissolved therein. The resultant mixture was stirred at 12,000 rpm under high shearing force by means of a TK type homomixer to form droplets of the polymerizable monomer composition. The thus-prepared aqueous 15 dispersion containing droplets of the polymerizable monomer composition was charged into a reactor equipped with an agitating blade to initiate a polymerization reaction at 90°C. After the reaction was continuously conducted for 8 hours, the 20 reaction was stopped to obtain an aqueous dispersion (pH=11) of polymer particles.

While stirring the above-obtained aqueous dispersion of the polymer particles, the pH of the aqueous dispersion was adjusted to about 5.5 with 25 sulfuric acid to conduct acid washing (25°C, 10 minutes). Filtration and hydration were then

conducted, and washing water was sprayed on the  
residue after the dehydration to conduct water  
washing. Thereafter, the thus-treated residue was  
dried for 2 days by a dryer (at 45°C) to obtain  
5 polymer particles.

(6) Developer (Toner):

To 100 parts of the polymer particles  
obtained above, were added 1.2 parts of silica  
10 ("HVK 2150", trade name; product of WACKER  
CHEMIE CO.) subjected to a  
hydrophobicity-imparting treatment and having an  
average particle diameter of 8 nm, and they were  
mixed by means of a Henschel mixer to prepare a  
15 non-magnetic one-component developer (hereinafter  
referred to as "toner" merely). The volume average  
particle diameter of the polymer particles  
(polymerized toner) was 7.1  $\mu\text{m}$ . The characteristics  
of the thus obtained toner for electrostatic charge  
20 image development, the resulting images, and so on  
were evaluated as in Example 1. The results are  
shown in Table 1.

Evaluation of toner for electrostatic charge image  
25 development

(1) Particle diameter of toner

The volume average particle diameter ( $D_v$ ) of toner particles and the particle diameter distribution ( $D_v/D_p$ ), i.e., the ratio of the volume average particle diameter ( $D_v$ ) to the number average particle diameter ( $D_p$ ), were measured by means of a particle diameter measuring device ("Multisizer", manufactured by Beckman Coulter Inc.). The measurement by the Multisizer was conducted under the following conditions:

- Aperture diameter: 100  $\mu\text{m}$ ;
- Medium: Isothone II; and
- Number of particles measured: 100,000 particles.

(2) Toner shape

As for the shape of toner particles, a photograph of the toner particles was taken with a scanning electron microscope; the photograph was read with a Nexus 9000 image processing unit; and a value obtained by dividing the length by the breadth ( $r_l/r_s$ ) of a toner was determined. Specifically, the number of toner particles subjected to the measurement was 100.

(3) Absorbance and color difference

A toner (0.2 g) was dispersed in 100 ml of THF.

The toner dispersion was filtered through a filter with a pore size of 0.45  $\mu\text{m}$  (GL Chromatodisc, nonaqueous, pore size: 0.45  $\mu\text{m}$ , manufactured by Kurabo Industries Ltd.) to remove insolubles and pigments with a large particle diameter. The dispersion from which insolubles and pigments with a large particle diameter are removed was transferred to a 1 cm thick cell for measuring transparency, and was subjected to the measurement of absorbance and chromaticity coordinates in the  $L^*a^*b^*$  color system by means of a spectrophotometer (trade name: SE-2000, manufactured by Nippon Denshoku Industries, Co., Ltd.). The color difference  $\Delta E$  between the dispersion and THF solvent was determined from the measured values according to the following equation:

$$\Delta E^* = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$$

#### (4) Image density

Printing paper was set in a commercially available non-magnetic-one-component developing type printer (trade name: Microline 3010c, manufactured by Oki Data Corporation). A toner was put in a developing device of the printer, and was left standing over a day and a night under the

(N/N) environment of a temperature of 23°C and a humidity of 50%. Then, printing was performed at a image density of 5%. After 10 sheets were printed, solid pattern was printed. The printed  
5 solid pattern was measured for image density using a color reflection densitometer (trade name: 404A, product of X-rite Inc.). Specifically, the amount of toner was 0.35 mg/cm<sup>2</sup>.

10 (5) Environmental durability and stability

Printing paper was set in a commercially available non-magnetic-one-component developing type printer (trade name: Microline 3010C, product of Oki Data Corporation), and a toner was put in a  
15 developing device of the printer. The toner was left standing over a day and a night under the (L/L) environment of a temperature of 10°C and a humidity of 20%, the (N/N) environment of a temperature of 23°C and a humidity of 50%, or  
20 (H/H) environment of a temperature of 35°C and a humidity of 80%. Then, printing was continuously performed at a image density of 5% from the beginning, and solid pattern was printed every 500 pieces of paper. The printed solid pattern was  
25 measured for image density using a color reflection densitometer (trade name: 404A, manufactured by

X-rite Inc.). At the same time, after each solid pattern was printed, plain pattern was printed and the printing was suspended. The developed toner on the photoconductive member was stripped off and  
5 collected by sticking with an adhesive tape (trade name: Scotch Mending Tape 810-3-18, manufactured by Sumitomo 3M Limited). Then the adhesive tape was peeled to stick it on a new sheet of paper to measure "hue (B)," using a spectrophotometer  
10 (trade name: SE2000, manufactured by Nippon Denshoku Industries Co., Ltd.). As a control, an adhesive tape alone was attached on another new sheet of paper to measure "hue (A)." Fog value was calculated and denoted as a color difference  $\Delta E^*$   
15 after hue values were expressed as a coordinate in an  $L^*a^*b^*$  space. Number of sheets was counted that can be continuously printed while maintaining the quality of images in which the image density is 1.3 or more and the fog value is 1 or less. The test  
20 printing was terminated when the number of sheets reached 10,000. Incidentally, larger number of sheets that can be continuously printed while maintaining the above described image quality is evaluated to show better environmental durability  
25 and stability.



(6) Gloss

The solid pattern printing image which was used for measuring the image density in (1) was used for measuring gloss by means of a gloss meter  
5 (trade name: VGS-SENSOR, manufactured by Nippon Denshoku Industries Co., Ltd.) at an angle of incidence on the image of 75°.

(7) Cockle

10 A toner in an amount of 0.6 mg/cm<sup>2</sup> was fixed on paper of A4 size, and the level of the warpage at the end of the paper was observed. The paper that has a smaller level of warpage is evaluated to have better toner characteristics.

Table 1

	Example	
	1	2
Dv ( $\mu\text{m}$ )	7.5	7.1
Dv/Dp	1.19	1.25
Circle degree	1.1	1.1
Maximum absorption wavelength (nm)	540	540
Absorbance	0.23	0.12
Color difference	6	0.3
Image density	1.24	0.71
Environmental durability and stability		
L/L	10000<	10000<
N/N	10000<	10000<
H/H	10000<	10000<
Gloss	58	50
Cockle	1.2	1.2